Process development for recycling rare earth from mining and urban waste materials

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Recycling targets

- Direct recycling of pre-consumer manufacturing REE scrap/residues
- Landfill mining of historic residues
- Urban mining of post-consumer waste (complex multi-materials matrices)
- Reprocessing of mining and metallurgical waste

Commercial recycling of REEs is extremely low. Less than 1% of the REEs were being recycled in 2011*

*Source: Binnemans et al. / J. of Cleaner Prod. 51 (2013), 1-22
Rare earth elements: recycling opportunities*

> Recycling is part of a threefold approach including also substitution & investment in primary mining
> REE are imported into the EU from a very limited number of producers
> Demand is high and steadily growing
> Recycling of REEs from spent products or mining/metallurgical waste, could provides a secondary supply
> However, closing the “REE loop” is a technical challenge, due to their specific uses and properties

Recycling of REEs is still at an early stage

*European parliament (2015) Recovery of Rare Earths from Electronic Wastes: An opportunity for High-Tech SMEs
Recycling REEs: specific challenges

> Development of dedicated techniques
  • To prevent from “poor” REE recycling due to routine techniques designed for primary resources (ores) and/or standard metals
  • To collect, sort and pre-treat WEEE specifically. Need for techniques focused on critical raw materials and particularly REEs

> Treatment
  • Few mechanical pre-treatment and sorting processes are able to liberate and separate the complex intermix of materials
  • Many components containing important resources are only partially sorted into the correct fractions. This leads to high losses of critical raw materials (dissipative processes)
  • After shredding, losses of REE = 100% because brittle magnets end up as fine particles attached to large steel parts in the steel industry (EAF*) and are lost (in slags) for any recovery process

*EAF : Electric Arc Furnace
## REEs recovery technologies

<table>
<thead>
<tr>
<th>Sources of REEs</th>
<th>Process</th>
<th>Technology readiness level</th>
<th>Existing at industrial level</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lamp phosphors (Eu, Tb, Y)</strong></td>
<td>Pre-processing + chemical attack of phosphors and recovery of REEs by precipitation or SX</td>
<td>Mature (still developing)</td>
<td>Yes (Solvay)</td>
</tr>
<tr>
<td><strong>Cathode Ray Tube phosphors (Eu)</strong></td>
<td>Chemical attack and solvent extraction</td>
<td>Limited research (declining interest ?)</td>
<td>No</td>
</tr>
</tbody>
</table>
| **Permanent Magnets (Nd, Pr Sm, Dy)** | - Hydrometallurgy  
- Gas-phase extraction  
- Reprocessing of alloys to magnets after $H_2$ decrepitation  
- Biometallurgy | Mature generally but still in lab scale  
Lab scale  
Lab scale  
Lab-scale | Investment project (Solvay)  
No  
No  
Planned pilot in 2014 |
| **NiMH batteries (La, Ce, Pr, Nd)** | Ultra High T°C smelting and hydro-pyro-metallurgy | Mature | Yes (UMICORE & SOLVAY) |
| **Optical Glass (La)** | Hydrometallurgy | Lab scale | No |
| **Glass polishing powder (Ce)** | Chemical process | Lab scale | No |

Source: Binnemans et al. (2013)
REE recycling process development: BRGM R&D projects

> **Urban waste**

- **VALOPLUS (achieved)**
  - Supported by ANR*
  - Recycling the luminescent powders used in low-energy light lamps
- **EXTRADE (ongoing)**
  - Supported by ANR
  - Recovery of REEs from permanent magnets in WEEE

> **Mining waste**

- **ENVIREEE (ongoing)**
  - EU-ERAMIN call

*ANR: French National research Agency
VALOPLUS
Valorization of used fluorescent powders

Contact point: Noureddine MENAD
n.menad@brgm.fr
Low energy lamps

> Compared to filament lamps
  - Energy consumption: 5 – 7 times lower
  - Lifetime: 6 – 12 times longer

> How it works?
Low energy lamps

> Composition

- **Old generation**
  - White phosphor => halophosphate

- **New generation:**
  - Red, blue and green phosphors => white light emission

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Formula</th>
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<tbody>
<tr>
<td>BAM</td>
<td>BaMgAl$<em>{10}$O$</em>{17}$ : Eu$^{2+}$</td>
</tr>
<tr>
<td>CAT</td>
<td>(Ce, Tb)MgAl$<em>{11}$O$</em>{19}$</td>
</tr>
<tr>
<td>CBT</td>
<td>(GdMg)B$<em>{5}$O$</em>{10}$:Ce$^{3+}$,Tb$^{3+}$</td>
</tr>
<tr>
<td>LAP</td>
<td>LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$</td>
</tr>
<tr>
<td>YOX</td>
<td>Y$_2$O$_3$:Eu$^{3+}$</td>
</tr>
</tbody>
</table>
Objectives

To develop innovative processes for the valorization of the phosphors throughout 2 approaches:

- Recovery of the pure phosphors
- Assessment of their performances for making new lamps
- Recovery of the REEs

*CFL: Compact Fluorescent Lamp
### VALOPLUS Process scheme

**Classification (hydrocyclone)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (in %)</th>
<th>Recovery rate (in %)</th>
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</thead>
<tbody>
<tr>
<td>Halophosphate</td>
<td>67</td>
<td>60.1</td>
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<tr>
<td>BAM</td>
<td>3.5</td>
<td>80.8</td>
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<tr>
<td>CAT</td>
<td>4</td>
<td>78.3</td>
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<tr>
<td>LAP</td>
<td>4</td>
<td>78.3</td>
</tr>
<tr>
<td>CBT</td>
<td>4</td>
<td>61.6</td>
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<tr>
<td>Y-Eu</td>
<td>16.5</td>
<td>78.8</td>
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</table>

**Magnetic separation 1**

<table>
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<tr>
<th>Element</th>
<th>Value (in %)</th>
<th>Recovery rate (in % of &lt; 10µm)</th>
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<tbody>
<tr>
<td>Halophosphate</td>
<td>68</td>
<td>36.2</td>
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<tr>
<td>BAM</td>
<td>4</td>
<td>27.2</td>
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<td>CAT</td>
<td>3</td>
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<td>LAP</td>
<td>10</td>
<td>84.8</td>
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<td>CBT</td>
<td>4</td>
<td>69.1</td>
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<tr>
<td>Y-Eu</td>
<td>11</td>
<td>21.9</td>
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**Magnetic separation 2**

<table>
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<th>Element</th>
<th>Value (in %)</th>
<th>Recovery rate (in % of &lt; 10µm)</th>
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<tbody>
<tr>
<td>Halophosphate</td>
<td>39</td>
<td>11.1</td>
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<td>BAM</td>
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<td>7.5</td>
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<td>80.0</td>
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<tr>
<td>Y-Eu</td>
<td>4</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**Flotation**

- YOX concentrate
- BAM concentrate
- Halo

**Doctoral thesis in progress BRGM/University of Lorraine – Flotation of ultrafine particles**
Main results

> Sampling of 6 sites and characterization of the collected samples
  • Phosphors are contained in the fine fraction

> Study on separation processes both on mechanisms and on experimental tests
  • Definition of a flowsheet for the separation and concentration of the phosphors/rare earth

> Evaluation of the quality of the recovered products
  • Positive results

> Patent pending (BRGM, SOLVAY, VEOLIA, University of Lorraine – 10/07/2014)
EXTRADE

Recovery of REEs from permanent magnets in WEEE

Contact point: Noureddine MENAD
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http://extrade.brgm.fr
REEs containing components in WEEE

Hard Disk Drives

Loudspeakers

Small electric motors
EXTRADE process

WEEE

Depollution

Recovery of magnets

Thermal treatment

Shredding

Selective extraction of REE

WEEE to toxic components

Iron Scraps

Plastics and others

Non ferrous metals

Eddy current Separation

Magnetic separation

Manual sorting

Selective extraction of REE

New magnets

Magnetization

Plastics and others

Non ferrous metals

Iron Scraps

Milling

Shredding

EXTRADE process

Routine Process

EXTRADE
Sampling of WEEE

Manual sorting of HDD

Loudspeaker shredding
Characterization

HDD characterization

Number of HDD

Mass % of permanent magnet

Number of HDD

Mass % of permanent magnet

Geosciences pour une Terre durable
Recycling process units

> Thermal treatment (demagnetization)
> Electrical (high-voltage electric pulses) and mechanical treatment to recover magnets from the computer system unit
> Route 1 – elaboration of new magnets with recycled magnets powder (short loop)
  - Separation of Ni coating from NdFeB magnets
    - Mechanical treatment
    - Chemical treatment: solvo-thermal decrepitation
    - Press-molding in magnetic field / sintering / magnetization
> Route 2 – extraction of REE using innovative hydrometallurgical techniques
  - Weak & cheap acid selective dissolution
  - Selective recovery of REE using biomaterials
> 2 patents in progress + 2 Soleau envelopes
ENVIREE  (Started March 2015)
ENVIRONMENTALLY friendly and efficient methods for extraction of Rare Earth Elements from secondary sources

Contact point: Yannick MENARD
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Context, objectives & topics

Tailings and other by-products from previous mining activities can hold significant amount of critical metals including REE

ENVIREE project is aimed at completing the picture of effective REE supply within Europe by addressing exploitation of specific secondary sources (mining and industrial waste)

Topics

• Identification/characterization/sampling of most suitable 2nd resources
• Mineral processing
  — Enhanced comminution
  — centrifugal concentration, multi-gravity separations, magnetic sep, column flotation
• Bio-Hydro-metallurgy
  — Bioleaching, selective oxidative leaching, use of strong halide solutions
  — New technologies for recovery of REE and better utilization of natural resources
  — Separation of REE using ionic liquids
  — Selective recovery using membrane contactors (grafted polymers, inorganic resins…)
Consortium – 11 partners, 8 countries

<table>
<thead>
<tr>
<th>Partner</th>
<th>Country</th>
<th>Contact person</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHALMERS</td>
<td>SE</td>
<td>Christian Ekberg (coordinator)</td>
</tr>
<tr>
<td>CEA</td>
<td>FR</td>
<td>Stéphane Bourg</td>
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<tr>
<td>BRGM</td>
<td>FR</td>
<td>Yannick Menard</td>
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<tr>
<td>AGH</td>
<td>PL</td>
<td>Katarzyna Grzesik</td>
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<tr>
<td>SAVONA PROJECT</td>
<td>PL</td>
<td>Slawomir Duda</td>
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<td>Catalin-Gabriel Borcia</td>
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<td>Maria Isabel Flausino de Paiva</td>
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<tr>
<td>KIT</td>
<td>DE</td>
<td>Andreas Geist</td>
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</table>
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You are welcome to visit our 2000 m² technology development facility